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Influence of oxygen doping on critical fields in MgB_2 bulk superconductors

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Abstract. In this work we studied the influence of SnO_2 doping on the critical fields and temperatures of MgB_2 bulk samples. Bulk samples were made by mixing *ex-situ* MgB_2 powder with 5 wt% SnO_2 powder and then pressing the mixed powders into pellets using a pressure of 2000 psi. The bulk pellets were sintered at 900°C in a furnace under flowing Ar. The samples were quenched to room temperature after dwelling at 900°C for 5h. XRD, SEM, and magnetic measurements were made on doped and control samples. XRD showed a decomposition of the SnO_2 and very slight reductions in the a-axis and c-axis lattice parameters of the MgB_2 phase. *M-T* (Magnetization-Temperature) curves showed a decrease in B_{c2} of approximately 1 T in the temperature range of 24 K - 39 K with SnO_2 additions as compared to the control samples.

1. Introduction

MgB_2 superconducting materials are of significant interest because of their relatively high critical temperature (~ 39 K), low cost, and simple two-gap nature. MgB_2 has strong interest for low to moderate field (0-3 T) applications in the 4-30 K temperature range, including MRI [1,2], superconducting motors and generators [3,4], and fault current limiters [5]. However, high field applications are limited by its relatively low upper critical field (B_{C2}) and low irreversible field (B_{irr}) which leads to low critical current densities (J_c) at high magnetic fields as compared to Nb_3Sn or YBCO. Much research has focused on the chemical doping of MgB_2 aimed at increasing either critical fields, critical currents, or both [6-13]. The most successful dopant has been C, added directly or as a compound, which releases C during reaction, which increases B_{C2} [12-13]. A few other dopants have been investigated which may add small amounts of flux pinning [14-15], but the increases in J_c were marginal since most dopants (except C) tend to segregate at grain boundaries. Some promising work on Dy_2O_3 has shown increases in J_c, although the mechanism is not fully clear [16-19]. However, a certain level of nanoscale intragrain defects were observed [17] in Dy_2O_3 doped MgB_2. In any case, the critical field increases seen in bulk and wire samples, while significant, have not reached the levels seen in earlier doped thin film work where critical fields of around 60 T and higher were seen at 4.2 K [7,8]. Oxygen doping appears to be part of the mechanism for the critical field increases seen in thin films, but so far, such increases have not been substantially translated to wires or bulks. Dou et al [6] used Sb_2O_3 powders as additions to in-situ route MgB_2 in an attempt to increase the critical fields, and in fact modest increases (about 1.3 T at 23.75 K) were seen in B_{C2}. In this work, we attempt to dope bulk samples with oxygen by including a SnO_2 powder additive to MgB_2 *ex-situ* powders. SnO_2 is an oxide which becomes unstable above 500 °C, and thus we will use this as a dopant in an attempt to provide an internal oxidation source for our MgB_2 *ex-situ* powder samples. We chose SnO_2 not only because of its above-noted decomposition, but also because Sn additions have been shown to be relatively benign additions to MgB_2 [20-21]. Below we carry out an initial study which attempts to increase the critical fields via oxygen doping using SnO_2 as the carrier.

2. Experimental details

Two MgB_2 samples were prepared using ex-situ powders which were pressed into pellets and then heat treated. One was made using pure pre-reacted MgB_2 powders (99% pure). A second, doped sample used pre-reacted MgB_2 powders (99% pure) mixed with 5wt% SnO_2 powders (99% pure) in order to investigate the influence of SnO_2 additions on the critical fields of MgB_2 bulks. First, the powders were mixed. Then the mixed powders were pressed into pellets (8.8 mm OD and 5 mm in height) under a load of 2000 psi at room temperature. The pellets were then sintered. The temperature was ramped up at 5ºC/h, then held at 900ºC under flowing Ar, and then the sample holder was pulled directly out of the furnace.

Microstructures of the MgB_2 pellets (after powderization) were characterized by scanning electron microscopy (SEM) using an FEI Sirion FEG in secondary mode. Powder X-ray diffraction (XRD) was performed using a Rigaku MiniFlex 600. XRD patterns were collected from 20 degrees to 80 degrees with a rate of 0.02 degree/step. The phases in the materials were identified, and lattice parameters were obtained for the MgB_2 phase.

Magnetization-Temperature (*M-T)* curves were measured on the samples from 5 K to 45 K using the vibrating sample magnetometer (VSM) mode of a Quantum Design Physical Property Measurement System (PPMS). In order to perform the measurements, the sample was first taken above T_c, a field of 0 T was applied, and the sample was cooled in zero field to 5 K. A field of 0.1 to 5 T was then applied, and the temperature slowly increased (5 K/h) until 45 K was reached; this constituted the zero field cooled measurement (ZFC). Once 45 K was reached, the field was left on while the temperature was again decreased through the transition and finally to 5 K; this was the field cooled (FC) measurement. The critical temperature at a given field was defined to be the point at which the deviation from the normal state magnetization (taken as a fraction of the total magnetization change during the ZFC measurement) was 5%. The irreversibility temperature was defined as the point at which the ZFC and FC measurements at a given field diverged [22]. Since T_c (T_{irr}) at a given field can be interpreted as B_{c2} (B_{irr}) at a given temperature, these results are presented as B_{c2} and B_{irr} vs T below.

3. Results and Discussions

3.1. Microstructure of the MgB_2 pellets

Figure 1 shows the SEM (secondary electron, SE mode) of the undoped sample (left) and the SE-SEM of the 5wt% SnO_2 doped sample (right). Both samples have been ground into fine powder, after which the powder was coated with a layer of gold for the SEM since there was charging effect due to bad connectivity in the samples. The grains are roughly equiaxed and SnO_2 additions did not make an appreciable change in the sample morphology. Furthermore, no noticeable secondary phases were seen from SEM images.

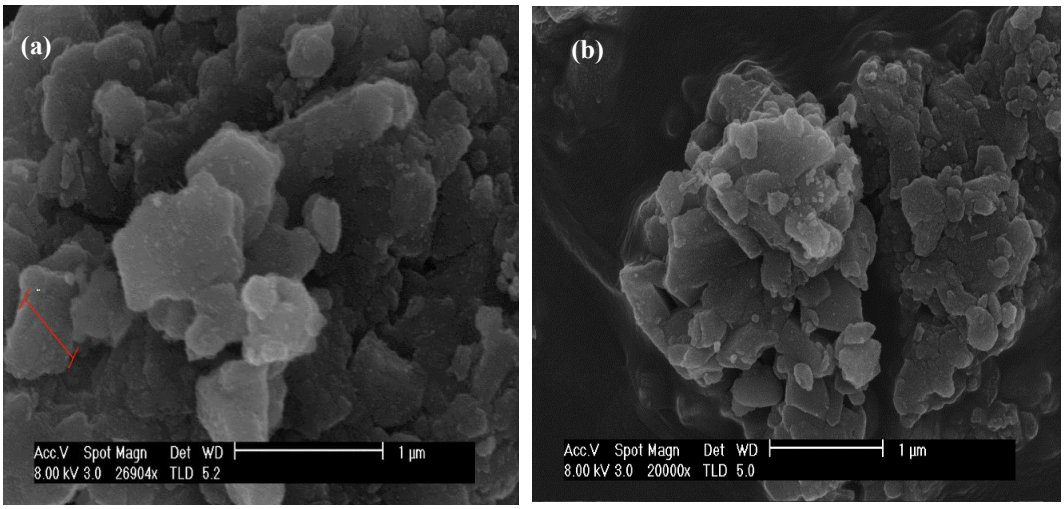

Figure 1 SEM images of undoped MgB_2 bulk sample (a) and the SnO_2 doped MgB_2 bulk sample (b). Pellet samples were powderized and gold coated before SEM.

3.2. Structure and phase analysis

Figure 2 shows the powder x-ray diffraction patters for the SnO_2 doped MgB_2 sample and the control sample. It can be seen that in both samples MgB_2 is a major phase, and that some MgO was also formed during the sintering process. From the doped sample pattern, we do not see SnO_2, but we do see free Sn, indicating the expected decomposition of SnO_2 to Sn and oxygen. Further, the active Mg reacted with Sn to form the intermetallic compound Mg_2Sn.

Based on the XRD data, lattice parameters for these samples were extracted. The lattice parameters of the undoped sample are a= 3.086 Å and c=3.525 Å, while those of the doped sample are: a=3.085 Å, and c=3.524 Å. There is no discernable lattice shift in a-axis and c-axis lattice parameters in MgB2 phases for the doped sample, which is different from Dou's work [3].

Our XRD results, while not speaking directly to oxygen doping per se, do allow us to look for MgB_2 lattice parameter shifts and the presence of gross second phases. Also, it allows us to look for presence of SnO_2 as well as free Sn – allowing us to see if SnO_2 has decomposed.

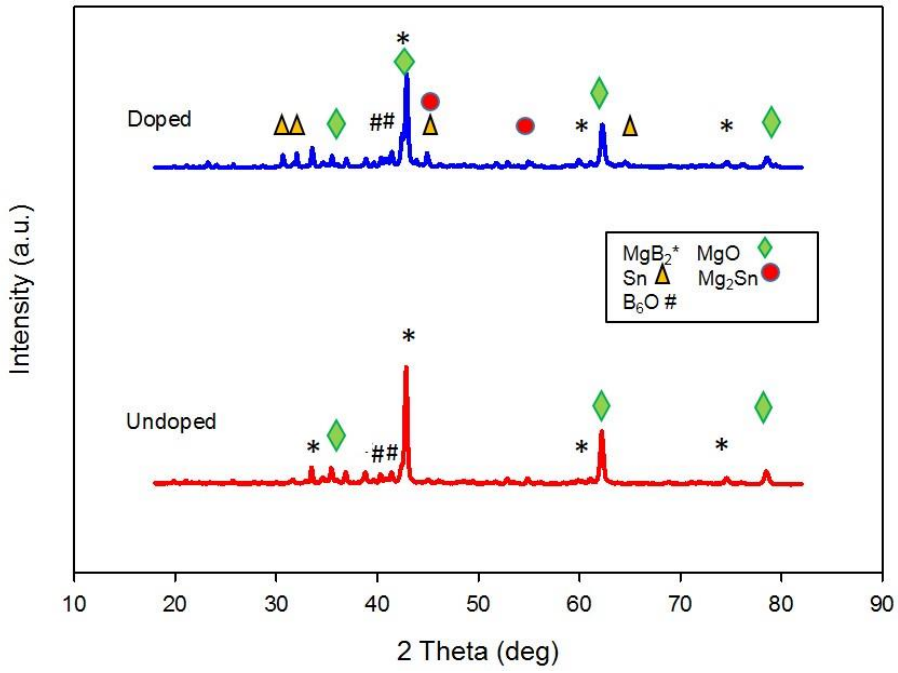

Figure 2 XRD patterns for 5wt% SnO_2 doped MgB_2 and control MgB_2 samples.

3.3. Magnetic response of the MgB_2 pellets

B_{irr} and B_{c2} as a function of temperature for the 5 wt% SnO_2 doped MgB_2 and the control MgB_2 bulk samples are shown in Figure 3. From the graph, we can see that in the temperature window between 24 K and 39 K, the doped sample has lower upper critical fields and irreversible fields than the control. In the 24-39 K window, there is approximately 0.5 T reduction in B_{irr} and B_{c2} for the doped sample as compared to the undoped sample. This result is different from Dou's result [6], where Sb_2O_3 additions increased the B_{C2} from 4.1 T (undoped sample) to 5 T at 29.2 K. Thus, under our specific preparation conditions we observed a decrease in the critical fields (within the temperature window we explored), rather than an increase with SnO_2 doping. This work only explored one doping level and one reaction heat treatment (HT), so we may not have found the optimum conditions. Also, we used an ex-situ route, rather than an in-situ one, and this may be an important factor.

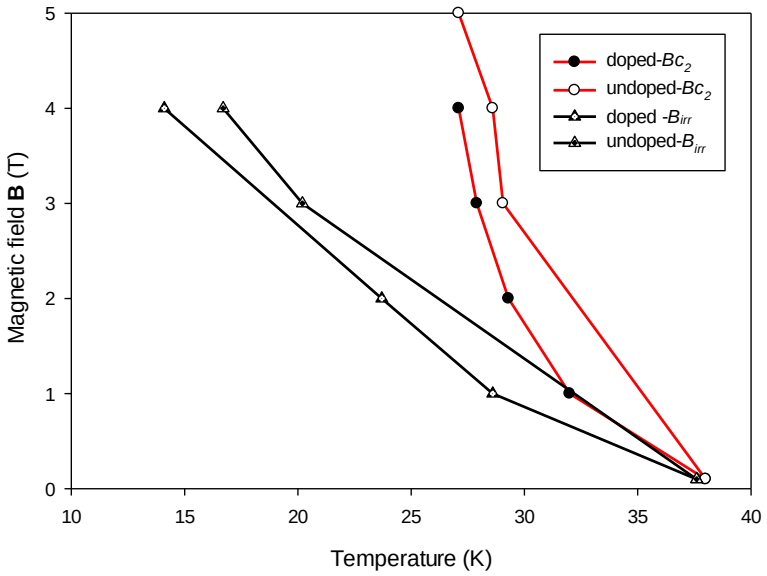

Figure 3 Temperature dependence of B_{c2} and B_{irr} of pure MgB_2 sample and SnO_2 doped sample.

4. Conclusion

An MgB_2 bulk sample has been fabricated with 5 wt% SnO_2 doping using an *ex-situ* processing route, and it has been compared to a control sample. SEM performed on the samples after powderizing shows similar grain structure in the doped and control sample. XRD measurements on the doped sample show no SnO_2, but the presence of free Sn, indicating the decomposition of SnO_2 during the reaction HT. XRD measurements show little or no change in c-axis lattice parameter, suggesting a lack of significant incorporation of oxygen into the lattice. A slight decrease in B_{c2} and B_{irr} was observed in the 24 K-39 K range. Addition of SnO_2 has slightly decreased B_{c2} and B_{irr} of MgB_2 given our particular preparation conditions of an ex-situ route and a 900 °C reaction heat treatment. The mechanism is unclear, and may be connected either to the oxygen or the Sn from the decomposed SnO_2. We have only explored one reaction temperature and one reaction type (ex-situ), which leaves a large amount of parameter space to explore. Given the promising results seen with previous in-situ work [6], we think oxygen additions are worth further exploration.

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